CHAPTER - 6 P-BLOCK (Most imp chapter)

(7-8 marks) (Reasoning type question)

Group 16 O S Se Te Po

Group 17 F Cl Br I At

Group 18 He Ne Ar Kr Xe Rn

Group 16

1. Why does melting and boiling point increases down the group?

Atomic size increases so Van der Waals force increases with increase in atomic number.

2. Oxygen unexpectedly has low negative electron gain enthalpy?

a) Small size of O_2 so small electron cloud

b) Inter electronic repulsion on the incoming electron.

Sulphur has a greater tendency for catenation than oxygen?

3. Oxygen exist as gas while sulphur exist as solid. Why?

a) Small size, it forms $p\pi$-$p\pi$ bonds and form diatomic O_2 molecule.

b) Intermolecular forces are weak Van der Waal forces which causes it to exist as diatomic.

a) Sulphur does not form double bonds and exist as puckered structure held by covalent bonds and exists as polyatomic.

4. Large difference in melting and boiling point of O_2 and S_8? Due to their atomicity O_2 exist as diatomic molecule whereas S_8 exist as polyatomic molecule.

5. On going down the group stability of -2 O.S decreases?
Down the group stability of -2 O.S decreases due to decrease in electronegativity

6. Bond angle in hydrides decreases on going down the group?
Size of central metal atom increases and electronegativity decreases on going down the group so force of repulsion between bonded pair of electron ~~increases~~ decreases.
Decreasing order of bond angle
$H_2O > H_2S > H_2Se > H_2Te$

7. Acidic character increases down the group. why?
a) Size of central metal atom increases and distance with hydrogen atom increases on going down the group.
b) Bond length increases and bond dissociation enthalpy decreases.
Decreasing order of acidic character.
$H_2Te > H_2Se > H_2S > H_2O$

8. Thermal stability on going down the group decreases?
a) Size of central metal atom increases ∴ tendency to form stable covalent bond with H_2 decreases.
Decreasing thermal stability
$H_2O > H_2S > H_2Se > H_2Te$

9. Reducing character of hydrides increases down the group. Why?
a) Thermal stability decreases down the group.
Greater is unstability, greater its reducing character.
Decreasing reducing character
$H_2Te > H_2Se > H_2S > H_2O$

$Al_2O_3 + 6HCl + 9H_2O \longrightarrow 2[Al(H_2O)_6]^{3+} + 6Cl^-$

$Al_2O_3 + 6NaOH + 3H_2O \longrightarrow 2[Na_3[Al(OH)_6]]$

3. Why does O_3 act as powerful oxidising agent?

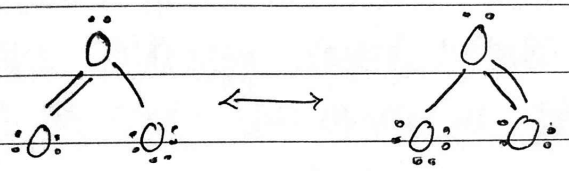
a) Higher energy content.

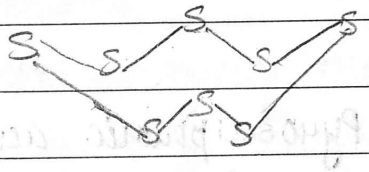
b) It easily decomposes into nascent oxygen.

$$O_3 \longrightarrow O_2 + O$$

$$PbS + 2O_3 \longrightarrow PbSO_4 + O_2$$

$$2I^- + H_2O + O_3 \longrightarrow I_2 + 2OH^- + O_2$$





Allotropic forms of sulphur.

i) Rhombic sulphur (α-sulphur) stable below 369 K

ii) Monoclinic sulphur (β-sulphur) stable above 369 K

At 369 K both forms co-exist and are stable so this temperature is called transition temperature.

* S_2 is paramagnetic It has two unpaired electrons in antibonding orbitals

$$SO_2 + 2O_2 \longrightarrow 2SO_3$$

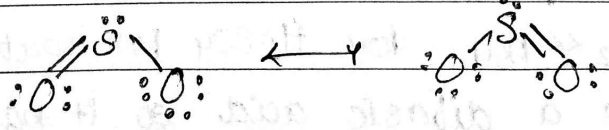
$$SO_2 + Cl_2 \longrightarrow SO_2Cl_2 \quad \text{(Sulphuryl chloride)}$$

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5S_2O_2 + 2MnO_4^- + 2H_2O \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$$

(Moist)

Fe



Quantitative method for estimating O_3 gas - when ozone reacts with an excess of KI soln buffered with a borate buffer iodine is liberated which is titrated against a standard solution of sodium thiosulphate.

10. SO_2 is reducing while TeO_2 is an oxidising agent?

a) +6 oxidation state of S is more stable than +4 oxidation state ∴ SO_2 is reducing agent.

b) Stability of +6 O.S decreases down the group so TeO_2 is oxidising agent.

11. SF_6 is extremely stable and chemically inert. Why?

a) The six F atoms protect the sulphur atom from attack by reagent to such an extent that most favourable reaction hydrolysis do not occur.

b) For steric reason (small size) it is stable.
SF_6 is sterically protected

12. Why is H_2O a liquid and H_2S a gas?
In H_2O molecules the force of attraction between O_2 and H_2 is hydrogen bonding and in case of H_2S it is Van der Waal force since Hydrogen bonding is stronger than van der Waal force.

$2KClO_3 \longrightarrow 2KCl + 3O_2$

$2Ag_2O \longrightarrow 4Ag + O_2$

$2Pb_3O_4 \longrightarrow 6PbO + O_2$

$2HgO \longrightarrow 2Hg + O_2$

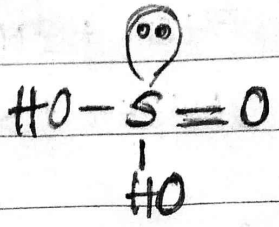
$2PbO_2 \longrightarrow 2PbO + O_2$

*. O_2 is paramagnetic

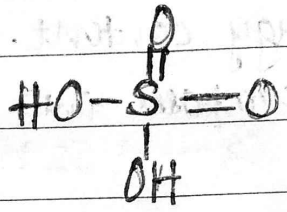
Acidic Oxides - (SO_2, CO_2, N_2O_5, Cl_2O_7, Mn_2O_7, CrO_3, V_2O_5)
Basic Oxides - Na_2O, CaO, BaO
Neutral Oxides - CO, NO, N_2O

Oxoacids of sulphur

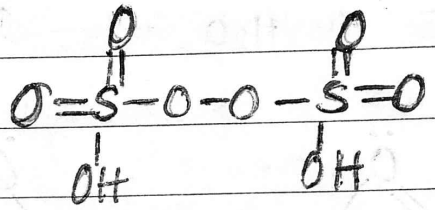
Sulphurous acid (H_2SO_3)



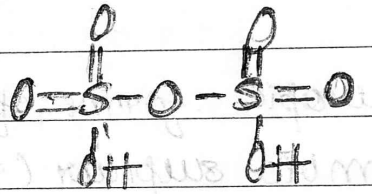
Sulphuric acid (H_2SO_4)



Peroxodisulphuric acid ($H_2S_2O_8$)



Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)



14. What are favourable conditions for maximum yield of H_2SO_4 in contact process?

Low temperature and high pressure are favourable condition because the reaction is exothermic, reversible and leads to decrease in volume.

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 12C + 11\,H_2O$$

15. Why $Ka_2 << Ka_1$ for H_2SO_4 in water?

a) H_2SO_4 is a dibasic acid so it has strong value of Ka_1 due to its ionization to H_3O^+ and HSO_4^-

b) $Ka_2 << Ka_1$ because a neutral H_2SO_4 has higher tendency to lose a proton than the negatively charged HSO_4^-.

16. SF_6 is known but SH_6 is not known. Explain

Fluorine is highly electronegative and can easily cause promotion of electrons from filled to the vacant 3d-orbitals. However, hydrogen is less electronegative. Therefore it does not cause the promotion of electrons. Thus SF_6 is known but SH_6 is not known.

17. Why halogens are coloured?

a) Due to absorption of radiation in visible region which results in the excitation of outer electron to higher energy level within the molecule or to the ~~outer~~ orbit of the element with which it forms compound.

18. Fluorine have low bond dissociation enthalpy than Chlorine Large electron-electron repulsion among the lone pairs in F_2 where they are much closer to each other.

19. Fluorine is a stronger oxidising agent than chlorine. Why?

a) Due to low bond dissociation enthalpy

b) Due to high hydration enthalpy of F^-

Born-Haber cycle
1. dissociation
2. low EGE
3. High hydration enthalpy

$$2F_2 + 2H_2O \longrightarrow 4F^- + 4H^+ + O_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

$$4I^- + 4H^+ + O_2 \longrightarrow 2I_2 + 2H_2O$$

Decreasing bond dissociation enthalpy.

$HF > HCl > HBr > HI$

20 Thermal stability of H-X compound decreases down the group?

As we move down the group bond strength decreases and therefore tendency to form stable covalent bond decreases.

Decreasing order.

$HF > HCl > HBr > HI$

21. On going down the group reducing character increases?

a) Thermal stability decreases down the group.

∴ Greater is the unstability, greater is reducing character.

Decreasing order

HF > HCl > HBr > HI HI > HBr > HCl > HF

HF is not a reducing agent

22. Acidic character increases down the group?

a) Bond dissociation decreases down the group so it can easily lose one H^+ ion to show acidic character.

Decreasing order

HI > HBr > HCl > HF

23. Decreasing order of reactivity towards oxygen -

I > Cl > Br

Iodine - oxygen bond is stable because of greater polarizability of I

Chlorine - oxygen bond is stable due to multiple bond formation involving d-orbitals of Cl atom

I_2O_5 - Good oxidising agent.

ClO_2 - Bleaching agent

Halide in higher O.S - More covalent than Low O.S.

$MnO_2 + 4HCl \longleftrightarrow MnCl_2 + 2H_2O + Cl_2$

$MnO_2 + 4NaCl + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

Deacon's process

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

Action with ammonia

$$8NH_3 + 3Cl_2 \longrightarrow 6NH_4Cl + N_2$$

(excess)

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

(excess)

Reaction with alkali

$$2NaOH + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

(cold and dil)

$$6NaOH + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

(hot and conc)

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

24. Why does chlorine water loses its yellow colour?

Chlorine water loses its yellow colour due to the formation of HCl and HOCl.

HOCl is responsible for oxidising and bleaching properties of chlorine due to release nascent of oxygen.

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + 2Cl_2 \longrightarrow H_2SO_4 + 4HCl.$$

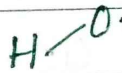
$$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$$

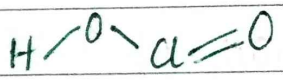
- Poisonous gases which can be prepared from chlorine are tear gas, mustard gas, phosgene.

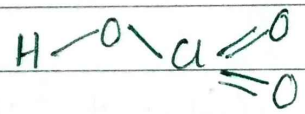
- Three parts of HCl and one part of HNO_3 forms aqua regia, which is used for dissolving noble metals.

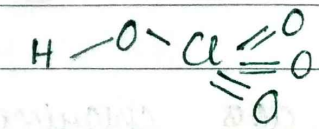
$$Au + 4H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$
$$Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

Oxoacids of chlorine

Hypochlorous acid 

chlorous acid 

chloric acid 

perchloric acid 

25. The acidic strength of oxoacids having same O-N of the halogen atom decreases with increase in atomic number?

The electronegativity of the halogen atom attached to the oxygen decreases in the order $Cl > Br > I$
∴ tendency to withdraw electron from oxygen atom towards itself decreases as a result the tendency to pull e^- from H_2 decreases so H^+ will not be easily liberated.

Decreasing order is

$$HClO > HBrO > HIO$$

26. With the increase in O.N of a particular halogen atom the acidic character of corresponding oxoacid increases?

This can be explained on the basis of Lowry Bronsted concept. According to this concept, a strong acid has a weak conjugate base and a weak ~~base~~ acid has a strong conjugate base. Greater is the stability of the conjugate base, lesser will be the attraction for proton and will behave as weaker base. Consequently weaker base will have strong acid and the decreasing order of stability of base is $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$

Decreasing order of acidic character is

$HClO_4 > HClO_3 > HClO_2 > HClO$

Interhalogen compound- XX'

(Larger size) ↓ ↳ smaller size

More electronegative

Nomenclature- X-full name X'-ide

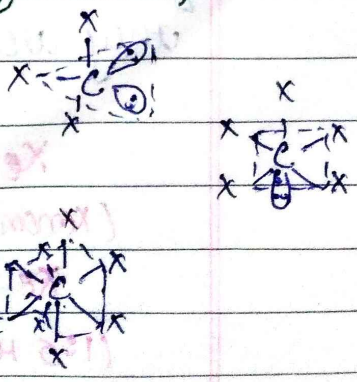
27. Interhalogen compounds are more reactive than halogen (except fluorine).

Because covalent bond between dissimilar atoms in interhalogen compounds is weaker than that between similar atoms in halogen atom (except fluorine).

XX_3 - Bent T shape (sp^3d)

XX_5 - Square pyramidal (sp^3d^2)

IF_7 - Pentagonal bipyramidal (sp^3d^3)



28. Fluorine exhibits only -1 O.S whereas other halogens exhibit positive O.S. why?

Fluorine is most electronegative element and cannot exhibit any positive O.S. On the other hand, other halogens are less electronegative and therefore can exhibit positive O.S. They also have vacant d-orbitals and hence can expand their octets.

29. HCl when reacts with finely divided iron forms ferrous chloride and not ferric chloride?

HCl when reacts with finely divided iron produce H_2 gas.

$$6HCl + 2Fe \longrightarrow 2FeCl_3 + 3H_2$$

Liberation of hydrogen prevents the formation of ferric chloride.

30. Out of noble gases, only xenon is known to form chemical compounds-

Because of its lowest ionization enthalpy among the noble gases.

31. Noble gases have very low boiling points. why?

Noble gases being monoatomic have no intermolecular forces except weak dispersion forces and therefore they are liquified at very low temperatures.

$$Xe + F_2 \longrightarrow XeF_2$$

(Xenon in excess)

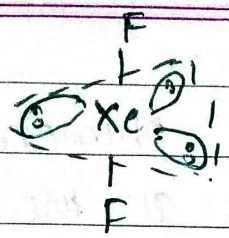
$$Xe + 2F_2 \longrightarrow XeF_4$$

(1:5 ratio)

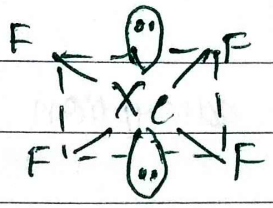
$$Xe + 3F_2 \longrightarrow XeF_6$$

(1:20 ratio)

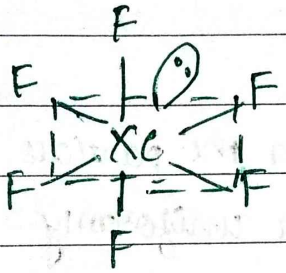
XeF_2
(Linear)



XeF_4
(Square planar)



XeF_6
(Distorted octahedral)



$2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

$XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$

$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$

$XeF_6 + MF \longrightarrow M^+ [XeF_7]^-$ M (Na, K, Rb or Cs)

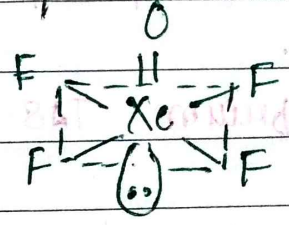
Complete hydrolysis

$6XeF_4 + 12H_2O \longrightarrow 2XeO_3 + 4Xe + 24HF + 3O_2$

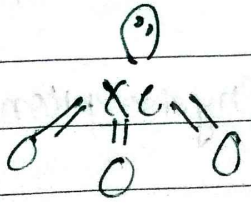
$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

Partial hydrolysis

$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$



$XeOF_4$
(Square pyramidal)



XeO_3
(pyramidal)

82. In the preparation of H_2SO_4 by contact process, why is SO_3 not absorbed directly in water to form H_2SO_4?

In Contact process SO_3 is not absorbed directly in water to form H_2SO_4 because the reaction is highly exothermic, acid mist is formed Hence, the reaction becomes difficult to handle

88. Explain why ClF_3 exists but FCl_3 does not exist?

Existance of ClF_3 and FCl_3 can be explained on the basis of size of central atom. Because fluorine is more electronegative as compared to chlorine and has smaller size. Thus, one large Cl atom can accomodate three smaller F atom but reverse is not true.

84. SF_6 is known but SCl_6 is not. why?

Fluorine atom is smaller in size so, six F^- ions can surround a sulphur atom. The case is not so with chlorine atom due to its large size. So, SF_6 is known but SCl_6 is

not known due to interionic repulsion between larger Cl^- ions.

35. Explain why Ozone is thermodynamically less stable than oxygen?

Ozone is thermodynamically less stable than O_2 because its decomposition into O_2 results in the liberation of heat and an increase in entropy. These two effects reinforce each other, resulting in larger negative Gibbs energy change for its conversion into O_2

- SO_2 dilute solution act as an disinfectant.
- SO_2 acts as bleaching agent in moist conditions.
- Peroxoacid have $-O-O-$ bond. (H_2SO_5 and $H_2S_2O_8$)
- SF_4 – see-saw shape.

36. SO_2 can act as both oxidising and reducing agent but H_2S only acts as reducing agents why?

In SO_2 O.S of sulphur is +4 which lies between (-2) and (+6) so it can increase or decrease. while in H_2S O.S of sulphur is (-2) which is minimum and it can only increase in H_2S.

Why Sulphur has greater tendency for catenation than oxygen?

Ans- Bond energy of S-S bond is greater than O-O bond! Due to small size of O_2 atom there is greater lp-bp repulsion in O-O, resulting in weakening of O-O bond than in S-S bond.

Why bleaching action of chlorine is permanent

Ans- Because the bleaching action is due to oxidation of HOCl.

Explain why insipte of nearly same electronegativity, oxygen forms hydrogen bonding while chlorine does not.

Ans - Oxygen has smaller size than chlorine. Smaller size of oxygen favours hydrogen bonding.